UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Analytical Chemistry Section
Building 306, BARC-East
Beltsville, Maryland 20705

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MAY 30 1989

MEMORANDUM

SUBJECT: PP#7E3489 - CGA-154281 on Corn Forage
Method Validation Report

FROM: Douglas M. Swineford, Chemist
Analytical Chemistry Section

THRU: Warren R. Bontoyan, Head
Analytical Chemistry Section

THRU: Donald A. Marlow, Chief
Analytical Chemistry Branch

TO: Robert Quick, Section Head
Tolerance Petition Section II
Dietary Exposure Branch
Health Effects Division (TS-769C)

INTRODUCTION

The Analytical Chemistry Branch was requested to run a method trial on the chemical CGA-154281. The Ciba-Geigy Corp. Method, "Ciba-Geigy Report #AG-536-A", Analytical Method for the Determination of CGA-154281 in Crops by Gas Chromatography was followed for the analysis of corn forage spiked at the 0.01 ppm level.

METHOD SUMMARY

A homogenous sample of corn forage was refluxed for 1.5 hours with 9:1 acetonitrile:water and filtered prior to taking an aliquot and partitioning with hexane in a water and saturated NaCl solution. The sample is eluted through a Florisil Sep Pak and analyzed by capillary gas chromatography using a DB-5 column and nitrogen - phosphorous detector.

COMMENTS

1. The submitted method for the quantitative analysis of CGA-154281 indicated that for the method to be successful it is imperative for the gas chromatographic (G.C.) standard used for quantitation be made with 20% dodecane in iso-octane to enhance the GC response of CGA-154281 as compared with the sample extract contained in 100% iso-octane (Method - Section II.H.5. and No. 4 and under comments for Laboratory Report No. 1 - Job #88-196). This is not a scientifically valid approach. Why not dilute the sample by some arbitrary amount to show good recovery data? Triple injections of the two standards analyzed in duplicate at the 1.0 ng level showed a 268% greater response for CGA-154281 made with 20% dodecane in iso-octane than the same amount of standard in 100% iso-octane.

2. G.C. chromatograms submitted with the method represent a very narrow window of approximately 2 minutes of retention time. This does not allow for a complete evaluation of the G.C. analytical data. The G.C. parameters show that the chromatograms are attenuated for the majority of the chromatographic run to show a level baseline and the attentuation is changed just prior to the single peak suggested for CAC-154281.

Our G.C. analyses of CGA-154281 Lot #ACK1, purity 99.4% obtained from the Environmental Protection Agency Pesticide Repository at Research Triangle Park, NC and evaluated at the same GC conditions as the submitted method except for the attenuation revealed several major chromatographic peaks representing approximately 10, 20 and 70% of the total peak area of the chromatogram for a 40 ng injection of the standard.

The method does not indicate the presence of multiple peaks in the CGA 154281 standard. This could result in serious error if the wrong peak is identified in the retention window.

3. Analysis of 25g aliquot of corn forage control and corn forage spiked at 0.01 and 0.02 ppm by the submitted method did not allow for the separation and accurate quantitation of CGA-154281 from the background of the corn forage matrix. The problem of high levels of interference for the analysis of corn fodder is also mentioned in comments number 6 of Ciba-Geigy - Job#88-196 (Report #1).

4. A skilled analyst with all the necessary equipment should be able to extract and clean-up a set of 6 samples in an 8 hour period. GC analysis can be done over night with an auto-sampler.

Because of the problems related to commetns #1, 2 and 3, we feel that this method is not suitable for enforcement purposes.

2

METHOD

Ciba-Geigy Method AG-536A, June 1988 "Analytical MEtod for the Determination of CGA-154281 in Crops by Capillary Gas Chromatography" by R. K. Williams.

Do not use control values for recovery corrections.

Do not report control values as 0.0 ppm. Accurately state your limit of detection. Please confirm the petitioner's claim for his limit of detection on the commodities listed below.

Commodity	Chemical Added	PPM Added	PPM Found	% Recovery
Corn Forage	None	Control		
	CGA-154281	0.01		
	CGA-154281	0.02		

Could not separate matrix interference from CGA-154281 at the 0.01 and 0.02 ppm level, therefore, no recovery data is provided.